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## A CHAMBER FOR SPECTROSCOPIC STUDIES OF ORGANIC VAPOURS

*A chamber designed to study photochemical and photophysical properties of organic vapours is described. Some results obtained in absorption and fluorescence experiments performed with it are presented.*

### 1. INTRODUCTION

For spectroscopic studies of organic vapours, different apparatus have been designed in order to produce the vapour, control and measure its temperature and pressure. They usually consist of an irradiation cell and a side arm, where vaporization of the product is carried out. Both compartments being made of pyrex or quartz, their heating requires the use of external metal furnaces. Temperatures are measured by thermocouples or platinum resistance thermometers placed in the furnaces walls [1, 5].

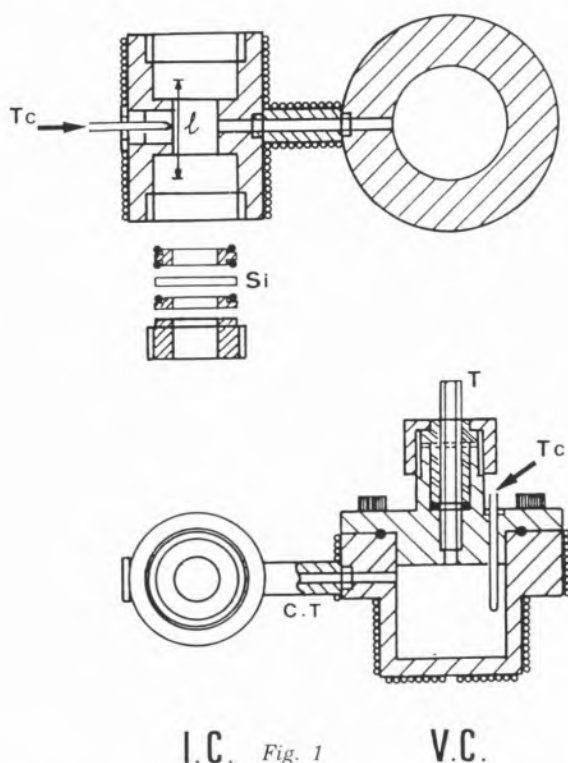
In the present work a chamber of this kind is described, which presents some interesting characteristics: as it is made of stainless steel, the walls themselves are the furnaces and the temperatures are taken inside the chamber, in the bulk vapour, which means that they are more accurate measures of the real temperatures. Of known dimensions, this chamber is suitable for experiments performed when only the vapour phase is present and in conditions of phase equilibrium (solid or liquid/vapour).

### 2. DESCRIPTION

The diagram of the chamber is displayed in Fig. 1. It also consists of two compartments: the vaporization cell (V. C.), where the solid or liquid is introduced and vaporized, and the irradiation cell (I. C.), where the vapour is irradiated. They communicate through a tube, whose dimensions were optimized in order to satisfy two contradictory conditions: be narrow and long enough so that temperature gradients were significant along the tube but not in either cell and be large and short enough to guarantee a rapid establishment of thermal equilibrium; the best compromise was obtained for a length of 15mm and a diameter of 2mm.

The vacuum sealing on the cover of the V. C. is assured by a pure gold O-ring. All the remaining O-rings indicated in Fig. 1 are in

fluoro-carbon rubber (Aerospace Material Specification 7278E), previously annealed to 150°C. They do not degase and are mechanically resistant to the temperatures and pressures of work.



I.C. Fig. 1 V.C.

Diagram of the vapour chamber: I. C. — irradiation cell; V. C. — vaporization cell; C. T. — communication tube; T — Pyrex tube which connects the chamber to a vacuum line;  $T_c$  — thermocouples;  $l$  — radiation path length; Si — fused silica windows; ● — pure gold O-ring; ○ — fluoro-carbon O-rings; o — thermocoax heating elements.

The vapour chamber may be connected to a vacuum line through the glass tube (T) placed on top of the V. C.

The interior volume of the chamber, including the glass tube up to the level where it is sealed, was determined both by calculations and by filling with water at 20°C as  $5.25 \pm 0.01$  cm<sup>3</sup>.

The two cells are thermostated separately by means of Thermocoax heaters (reference ZAZ Ac 10 from S. A. Sodern), made of nickel chromium 80/20, with a resistivity of  $108 \mu\Omega/\text{cm}$ , and with low resistance cold ends of nickel chromium tube with CuZr filling. The insulating material is high purity MgO and

the sheath of austenitic stainless steel. The outer diameter is 1.0 cm and the total length was conveniently dimensioned according to the power needed to heat each cell (the communicating tube was included, for this purpose, in the irradiation cell). The heating elements were coiled around the chambers and, to improve thermal contact, metal wrappers were fixed around the heating elements.

Temperatures are measured by Thermocoax thermocouples of iron-constantan, with 18-8 stainless steel sheath and characterized by an output voltage of approximately  $55 \mu\text{V}/^\circ\text{C}$ . Their external diameter is of 2mm. They are silver-brazed, respectively to the V. C. cover and to the wall of the I. C. (see Fig. 1), the hot junction being inserted in a suitable cavity not to interfere with the radiation path. The thermocouples are connected to Pastocomp temperature controllers (PD model) having a sensitivity higher than  $0.5^\circ\text{C}$  in the measured value.

Some care had to be taken in order to correct the thermocouples readings: as may be seen in Fig. 1, the hot junction was placed too close to the cell walls in the I. C., and so its information could be influenced by conduction through the thermocouple sheath. Tests were made placing a similar but insulated thermocouple in the bulk vapour, in the middle of radiation path. A curve of these last readings versus the values obtained with the brazed thermocouple was used as a calibration. The same kind of tests showed that this problem did not occur in the V. C..

Each system thermocouple-controller was calibrated separately by comparison with the readings of calibrated Hg thermometers immersed in water and in oil baths, for temperatures between 15 and 220°C, exactly in the same conditions as the thermocouples.

Fused silica windows were used in the I. C., but they can obviously be replaced by windows made of any other adequate material. The optical path length through the vapour, once the setting is complete, is  $17.60 \pm 0.05$  mm.

### 3. EXPERIMENTS PERFORMED WITH THE CHAMBER. RESULTS

As mentioned before, visible or UV absorption of organic vapours may be studied with this chamber at different temperatures, either at constant concentration either in equilibrium of phases (the concentration depending, in this case, on the temperatures of both cells [6]).

The first kind of measurements requires an accurate knowledge of the vapour concentration. In order to minimize the errors in such determination, the compound, previously degased, must be weighed under vacuum atmosphere in a microanalytical balance. As the weight of the whole chamber largely exceeds the capacity of such balances, an appropriate Pyrex device was designed for this purpose (see Fig. 2). It consists of a bulb (A) where the substance is introduced, a con-

nection to a vacuum line (D), where Viton O-rings are used, and a «Rotaflor» tap (B) with Teflon stopcock, to avoid any contaminations produced by the currently used vacuum grease.

To prepare the vapour samples, the following procedure is used: the device, previously cleaned, is evacuated to nearly  $10^{-4}$  Pa. After closing tap B, it is weighed in a microanalytical balance Mettler M5/S5 ( $W_A$ ). The piston is removed and an approximately known volume of the liquid (or weight, if a solid) is introduced in the bulb (A) through the top. It is then degased by the classic vacuum technique. After several freeze-pump-thaw cycles, (B) is closed and the weight of the whole apparatus is determined ( $W_B$ ). The bulb, immersed in liquid nitrogen, is sealed off at level C and introduced in the V. C., which is evacuated and also sealed. A ring in stainless steel with a sharp point has been previously placed on the bottom of V. C., just below the bulb, which may then be broken from the outside, by a mechanical impulse. Afterwards, vaporization carries out.

The vapour concentration in the chamber, C, is calculated by the simple expression:

$$C = \frac{(W_B - W_A) / MW}{V}$$

where MW is the compound molecular weight and V the total useful volume of the chamber ( $V = 5.193 \text{ cm}^3$ , after deducing the volumes of the glass sherds, the pointy piece and the thermocouples ends inside the cells).

Absorption spectra were recorded in Perkin Elmer Spectrophotometers, models 552 and Lambda 5. Fluorescence spectra were obtained in transmission, with a home-built spectrofluorometer [7], using a helium-cadmium ion laser from Spectra-Physics, model 185, as a source. Benzene Uvasol from Merck, purity > 99.7% and para-xylene puriss, from Fluka, purity > 99.5%, were used without further purification. Pyrene puriss, from Fluka was zone-refined before use.

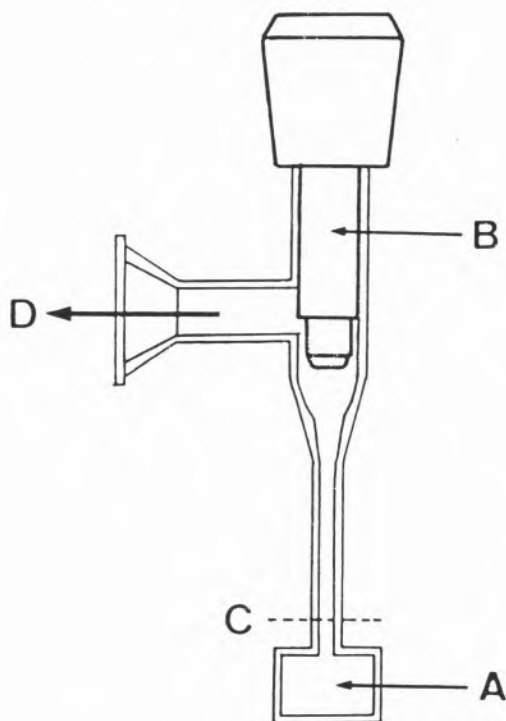


Fig. 2

Pyrex glass device to prepare the vapour samples: A — bulb where the product is introduced; B — Teflon stopcock; C — level where it is sealed off; D — connection to vacuum line.

**A**—Absorption spectra at constant vapour concentration were studied thermostating both cells at the same temperature:  $T(I. C.) = T(V. C.)$ . About twenty minutes after each temperature change, the reproducibility of the spectra was excellent, providing a good evidence for the stabilization inside the chamber.

The symmetry forbidden transition  ${}^1B_{2u} \leftarrow {}^1A_{1g}$  of benzene vapour, centered at  $\approx 260\text{nm}$ , has been studied in these conditions, as a function of temperature. Concentrations covered the range:  $1 \times 10^{-4}$  to  $5.5 \times 10^{-2}$  M and temperatures were changed from the minimum value corresponding to total vaporization of the product to 418 K. A similar study was carried out for para-xylene, in the same region of wavelengths. The intensity variation with temperature, expressed as a function of absorbance and of the spectra integrated area, as well as the dependence on temperature of the vibronic components of these electronic transitions have been reported elsewhere [8] and are still being studied in our laboratory. Here, just to illustrate the chamber's possibilities, we present some of the spectra obtained for benzene and para-xylene (Figs 3 and 4), where the variations of absorbance with temperature for different vibronic transitions are clearly brought out.

**B**—When working with saturated vapours and to avoid condensation on the walls of the I. C., it must be maintained at a slightly higher temperature than the V. C.:  $T(I. C.) > T(V. C.)$ . In this case, the amount of product introduced in the bulb need not to be known, providing it is in excess to guarantee an equilibrium of phases. In order to achieve stabilization after each change in the V. C. temperature (i. e., to obtain reproducible spectra), a period of about one hour must be respected. Twenty minutes proved to be enough when only the temperature of the I. C. was changed. These spectra were useful in the development of a method to determine

saturated vapour concentrations, as a function of the temperatures of both cells. That work, which involves the fitting of interesting molecular parameters, is reported elsewhere [6].

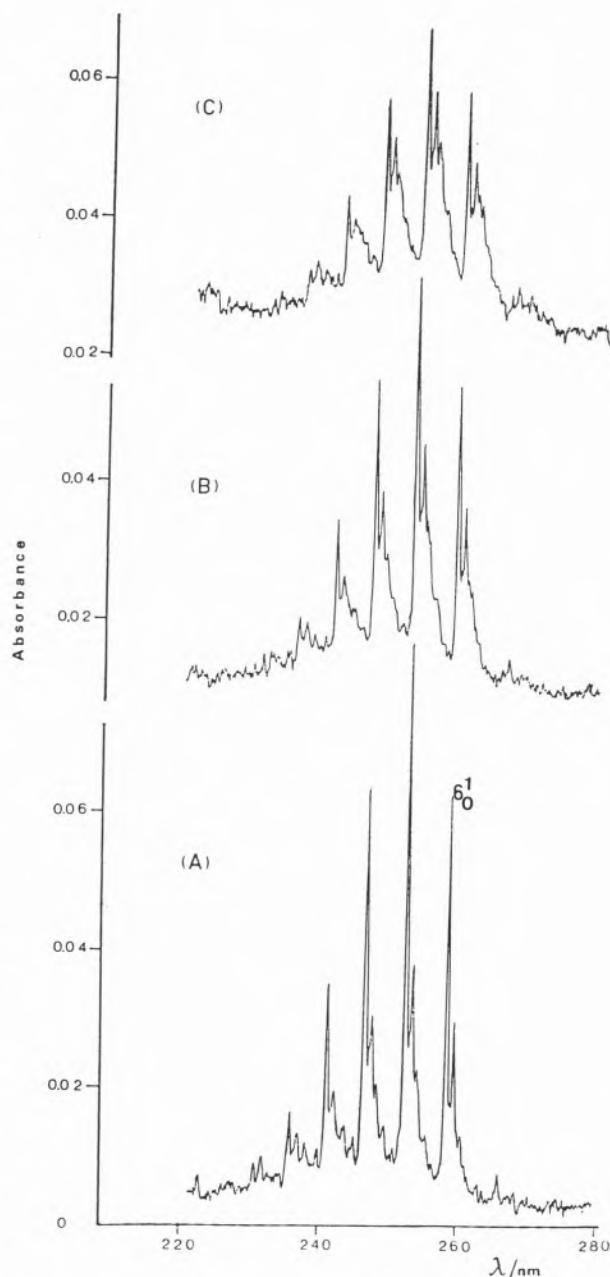


Fig. 3

Absorption spectra of benzene vapour (transition  ${}^1B_{2u} \leftarrow {}^1A_{1g}$ ) obtained for a concentration of  $1.5 \times 10^{-4}$  mol  $\text{dm}^{-3}$  at different temperatures: (A) —  $T = 303$  K; (B) —  $T = 353$  K; (C) —  $T = 403$  K.

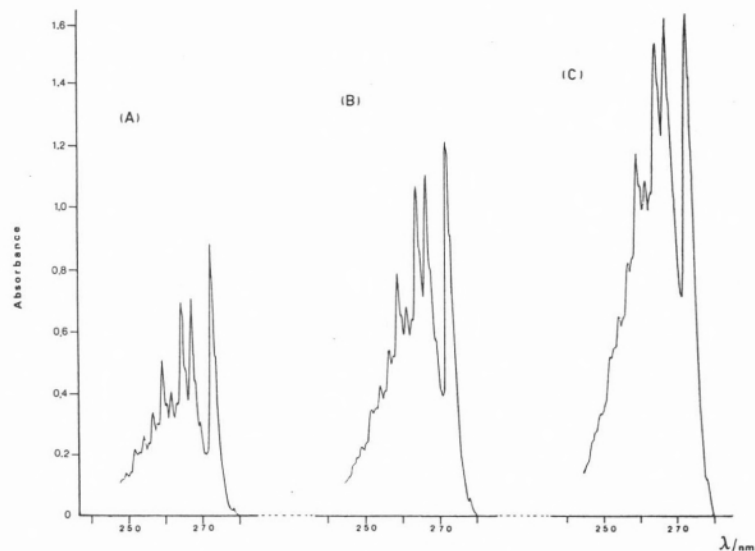


Fig. 4

Absorption spectra of para-xylene vapour for a concentration of  $9.8 \times 10^{-3} \text{ mol dm}^{-3}$ :

(A) -  $T = 335 \text{ K}$ ; (B) -  $T = 353 \text{ K}$ ; (C) -  $T = 413 \text{ K}$ ;

To test the convenience of the vapour chamber for working with low vapour pressure compounds (solids at normal temperature), absorption of saturated pyrene vapour to the

second excited singlet state and fluorescence from the first singlet state were also studied as functions of both temperatures. As may be observed from Fig. 5, a very good reso-

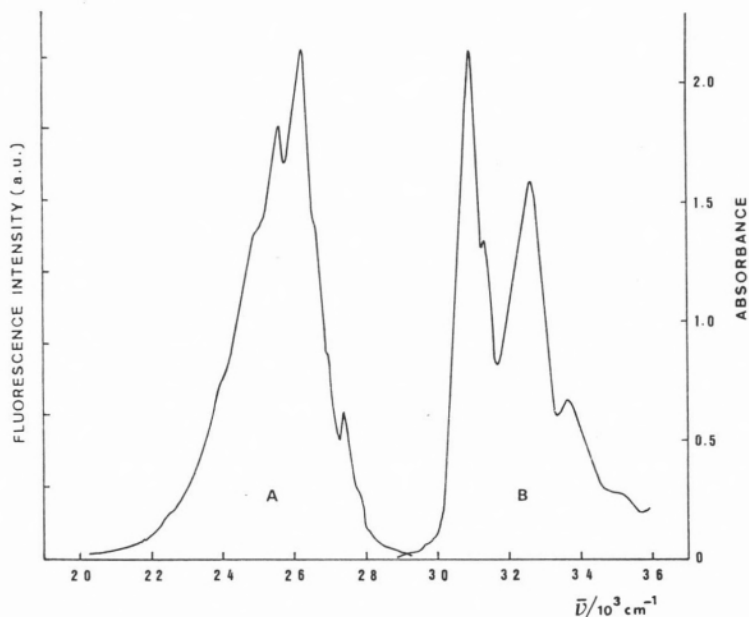


Fig. 5

**A** — Non corrected fluorescence spectrum of pyrene vapour excited at  $30769 \text{ cm}^{-1}$  ( $\lambda_{\text{exc}} = 3250 \text{ Å}$  of an He-Cd ion laser), for  $T(\text{V. C.}) = 469 \text{ K}$  and  $T(\text{I. C.}) = 498 \text{ K}$ .

**B** — Absorption of pyrene vapour to the second excited singlet state, for  $T(\text{V. C.}) = 469 \text{ K}$  and  $T(\text{I. C.}) = 498 \text{ K}$ .



lution was obtained for the fluorescence spectra when compared with others published [9, 10] (\*).

#### 4. CONCLUSION

The spectra obtained with the chamber described here, particularly in the case of benzene, have already been the subject of an extensive study [11]. Nevertheless, it is still of interest to improve the experimental conditions in which they are obtained, in order to clarify some questions related to the nature of the states involved and to the quenching mechanisms in the vapour phase. It seems clear that this chamber presents some advantages when compared to other similar apparatus: inherent to the fact that the walls themselves are the furnaces and that temperatures are taken in the bulk vapour, there is a more accurate control and knowledge of both temperatures. This allows the vapour concentration in the irradiation cell to be known more accurately, either for low concentration ranges (constant concentration experiments used concentrations as low as  $10^{-4}$  M) or for high concentrations (particularly when working in equilibrium of phases). Moreover, the excellent reproducibility of the spectra supplied a good evidence for the establishment of thermodynamical equilibrium at each temperature (or pair of temperatures) of work.

(\*) In both kinds of absorption experiments reported in this work, a base line was recorded and memorized in the spectrophotometer before breaking the Pyrex bulb containing the product.

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#### RESUMO

##### Uma câmara para estudo espectroscópico de vapores orgânicos

Descreve-se uma câmara em aço inóx, projectada para o estudo de propriedades fotoquímicas e fotofísicas de vapores orgânicos. Apresentam-se alguns resultados obtidos em experiências de espectroscopia de absorção e fluorescência.